

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
17 April 2003 (17.04.2003)

PCT

(10) International Publication Number
WO 03/031134 A1

- (51) International Patent Classification⁷: **B29B 15/08**, (74) Agent: NASH, David, Allan; Haseltine Lake, Imperial House, 15-19 Kingsway, London WC2B 6UD (GB).
B29C 47/10, B29K 23/00, 105/04
- (21) International Application Number: PCT/GB02/04599 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 10 October 2002 (10.10.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 0124324.5 10 October 2001 (10.10.2001) GB (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): IMERYS MINERALS LIMITED [GB/GB]; John Keay House, St Austell, Cornwall PL25 4DJ (GB).
- (72) Inventors; and
- (75) Inventors/Applicants (*for US only*): ANSARI, Deebea, Marjan [GB/GB]; 43 Carclew Street, Truro, Cornwall TR1 2DZ (GB). COLES, Alan, Edward [GB/GB]; Bosilliac, Penwarne Road, Mawnan Smith, Falmouth, Cornwall TR11 5EN (GB). LONGEVAL, Rudy, Antoine, Theofiel [BE/BE]; Denderhoutembaan 75B1, B-9400 Niove (BE).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: PROCESS FOR MAKING A MINERAL FILLED POLYMER COMPOSITION

(57) Abstract: There is disclosed a process for incorporating a particulate calcium carbonate filler in a thermoplastic polymer to form a calcium carbonate-filled polymer composition suitable for the preparation of breathable polymer film, said process comprising: (a) introducing the calcium carbonate into the polymer in a dry compacted form which has a bulk density greater than the maximum bulk density obtainable by subjecting an uncompacted sample of the calcium carbonate to tamping; and (b) mechanically treating the polymer to disperse the calcium carbonate uniformly therein. Also disclosed is an apparatus therefor comprising a compactor and an extruder which includes at least one inlet to which the compactor is connected.

WO 03/031134 A1

PROCESS FOR MAKING A MINERAL FILLED POLYMER COMPOSITIONDESCRIPTION OF THE INVENTIONField of the invention

5 The present invention relates to a process for making a calcium carbonate-filled thermoplastic polymer which is suitable for use in the manufacture of breathable film, and to an apparatus for carrying out making a calcium carbonate-filled thermoplastic polymer
10 composition.

Background of the Invention

Alkaline earth metal carbonates, particularly calcium carbonates are used as the particulate filler in end products comprising compositions incorporating
15 thermoplastic polymers, such as breathable film products. Such films are manufactured for a number of consumer products such as backing materials, plastic paper, house wrap, roofing membranes, grocery sacks, diapers, bandages, training pants, sanitary napkins,
20 surgical drapes, and surgical gowns. The compositions from which these films are made may include two basic components, the first being a thermoplastic polymer, usually a predominantly linear polyolefin polymer such as a linear low density polyethylene and the second
25 being an inorganic particulate filler such as calcium carbonate. A third component, namely a bonding or tackifying agent may often be present. These components are mixed and compounded together to form a compound or concentrate which is formed (usually in a subsequent
30 process) into a film layer using any one of a variety of

film-producing processes known to those of ordinary skill in the film making art including casting or blowing. Alternatively, the film may be laid down on a substrate such as paper or board in a process known as
5 extrusion coating.

After the film is fabricated into its desired form, it is then stretched, uniaxially or biaxially, by any of the well-known techniques in the art including by hydraulics, by pinch rolls moving at different rates, by
10 interdigitating rolls or by tentering, to make a porous, breathable film.

US Patent No. 5,827,917 discloses a method of incorporating a fine talcum powder into a material such as a thermoplastic material. The talcum powder is mixed
15 with water and a polyethylene glycol, a polypropylene glycol or a copolymer of these compounds and then pressed through dies and sectioned to obtain granules. The product granules obtained are incorporated in the thermoplastic material which is then subjected to
20 mechanical action to break up the granules.

US Patent No. 5,773,503 discloses a compacted mineral filler pellet in which mineral filler particles are combined with a compaction additive which is formed into pellets and dried. The compacted mineral filler
25 pellets may then be loaded into a thermoplastic polymeric compound and dispersed.

Apparatus for deaerating and densifying finely divided powders are known. Such devices are, for example, available from Universal Processes and Plants
30 Ltd, Storrington, England. In such devices, the finely

divided powder is introduced onto a slowly rotating and submerged filter drum which is subjected to an internal vacuum.

The article "Compounding compacted talc: some recent developments" dated 7th May 2001 appeared on the website www.specialchem.com. This article reports on how the use of compacted fillers increases bulk density and improves handling, feeding and incorporation of the fillers into the compound.

10 Summary of the Invention

In a first aspect, the present invention relates to a process for incorporating a particulate calcium carbonate filler in a thermoplastic polymer to form a calcium carbonate-filled polymer composition suitable for the preparation of breathable polymer film, said process comprising:

- (a) introducing the calcium carbonate into the polyolefin resin in a dry compacted form which has a bulk density greater than the maximum bulk density obtainable by subjecting an uncompact sample of the calcium carbonate to tamping; and
- (b) mechanically treating the polymer to disperse the calcium carbonate uniformly therein.

The calcium carbonate-filled polymer composition made by the processes of the present invention may be used to prepare breathable thermoplastic polymer film, and preferably breathable polyolefin film, in a known manner. Thus, the processes of the first aspect of the

present invention may comprise the following further steps:

optionally adjusting the polymer content of the calcium carbonate-filled polymer composition by mixing
5 it with additional polymer which may be the same as or different from the polymer of the composition;

extruding the calcium carbonate-filled polymer composition (optionally having an adjusted polymer composition) to form an intermediate film; and
10 stretching the intermediate film to form a stretched, breathable film

In a further aspect, the invention relates to an apparatus for making a calcium carbonate-filled thermoplastic polymer composition comprising:

15 a compactor for dry-compacting a source of particulate calcium carbonate supplied to it, said compactor being capable of compacting the calcium carbonate to a bulk density greater than the maximum bulk density obtainable by subjecting an
20 uncompact sample of the calcium carbonate to tamping; and

a compounder for compounding the particulate calcium carbonate and the polymer, which includes at least one inlet for receiving the
25 dry compacted calcium carbonate from the compactor and a flow of a thermoplastic polymer;

wherein the compactor is disposed to supply the compacted calcium carbonate to the compounder.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a tamping apparatus which may be used to determine the maximum tamped bulk density of a sample of calcium carbonate.

5 Figure 2 shows apparatus in accordance with one aspect of the invention for making a calcium carbonate-filled polymer composition.

Figures 3a-3e summarise the process conditions used in the compounding step of the examples.

10 DETAILED DESCRIPTION OF THE INVENTION

As described above, the present invention, in one aspect, relates to a process for incorporating a particulate calcium carbonate filler in a thermoplastic polymer to form a calcium carbonate-filled polymer
15 composition. In this process, the calcium carbonate is introduced into the polymer in a dry compacted form. The thus-formed composition is then mechanically treated to disperse the calcium carbonate uniformly therein. The dry compacted calcium carbonate has a bulk density
20 which is greater than the maximum bulk density obtainable by subjecting an uncompacted sample of the calcium carbonate to tamping.

It has been found that the throughput of such a process, before excessive dusting is observed, is
25 increased relative to a process in which a calcium carbonate which is not in a dry compacted form is used. Moreover, the dry compacted calcium carbonate is found to disperse well in the resin. In addition, when the calcium carbonate-filled polymer composition made in
30 accordance with the present invention is used to

manufacture breathable film, it has been found that the number of film defects is reduced.

In the process of the present invention, the calcium carbonate which is to be used as the filler is employed in a dry compacted form, and has a bulk density which is greater than the maximum bulk density obtainable by subjecting an uncompact sample of the calcium carbonate to tamping. As used herein, the term "tamping" means effecting a series of jolts or bumps to a container containing the sample of particulate calcium carbonate, without the application of any external pressure to the sample. When a sample of a dry calcium carbonate is tamped in this way, the volume which the material occupies reduces as a result of the differently sized particles packing together in a more efficient manner. After tamping for a period of time, the volume which the material occupies will reach a minimum, and the bulk density a maximum. The calcium carbonate which is to be introduced into the polymer resin in the process of the invention has a bulk density greater than this maximum bulk density obtained by tamping.

One tamping procedure which may be used is set forth in Appendix A below.

As mentioned above, the calcium carbonate filled polymer composition obtained by the process of the invention is suited for use in the manufacture of breathable polymer film. The calcium carbonates used as fillers for breathable films generally have a d_{50} ranging from 0.5 to 10 μ m, typically 1 to 2.5 μ m. The dry compacted bulk density for such materials may be,

- 7 -

for example, at least 50g/litre greater than the tamped bulk density, or in some embodiments at least 100g/litre greater than the tamped bulk density. Good results have been obtained with materials for which the dry compacted bulk density is of the order of about 150g/litre greater than the tamped bulk density.

The dry compacted calcium carbonate for use in the invention may be obtained by compressing the calcium carbonate material and optionally simultaneously subjecting the material to a vacuum in order to deaerate the material before the dry compacted material is collected. The pressure exerted and (optionally) the vacuum applied should be selected to produce a compacted, or densified, material which has a bulk density greater than that obtained by tamping (as defined above). For a relatively coarse calcium carbonate having a d_{50} (defined as the particle size value less than which there are 50% by weight of the particles) of about $2\mu\text{m}$ and a tamped bulk density of about 1400g/litre, it has been found that, without deaeration, a pressure of the order of 120g/cm^2 is required to obtain a bulk density of about 1500g/litre. With a deaeration pressure of about 10 inches Hg, a pressure of only 25g/cm^2 was needed whilst at 20 inches Hg, a pressure of 3g/cm^2 was sufficient to produce a bulk density of about 1500g/litre.

Examples of deaerating and densifying equipment for producing a dry compacted calcium carbonate which may be used in the invention are those available from Universal Processes and Plant Limited of Storrington, England.

- 8 -

This company sells a range of densifiers from the 160/220 unit which has a typical throughput up to about 900 kg/hr to the 520/750 unit which has a throughput from about 200 to 16,000 kg/hr. This equipment
5 generally includes a pair of counter-rotating drums which compact the particulate material as it passes between them. At least one of the drums is a filter drum, the inside of which has a reduced pressure applied to it to deaerate the particulate material as it passes
10 over the outside of the drum

The calcium carbonate is subjected to compaction in a dry form, that is to say without any added binder such as water which would tend to cause the particles of the calcium carbonate to agglomerate. The resultant
15 product, although compacted is nevertheless still relatively free flowing, albeit as a clumpy powder.

In the mechanical treatment step of the first aspect of the invention the mixture of ingredients is compounded to form a uniform blend. At this stage, in
20 addition to the polymer and the filler, other known optional ingredients conventionally employed in thermoplastic films may be introduced, e.g. one or more of bonding agents, plasticisers, lubricants, anti-oxidants, ultraviolet absorbers, dyes, colorants. A
25 bonding or tackifying agent, where employed, may facilitate bonding of the film after formation to another member, e.g. a non-woven fibrous layer, or one or more non-porous layers.

The polymer, the filler and, if necessary, other
30 optional additives, may be mixed by the use of a

- 9 -

suitable compounder/mixer and may be pelletized, e.g. by the use of a single screw extruder or a twin-screw extruder which forms strands which may be cut or broken into pellets. The compounder may have a single inlet
5 for introducing the compacted or densified calcium carbonate and the polymer together. Alternatively, separate inlets may be provided for the calcium carbonate and the polymer. Suitable compounders are available commercially, for example from Werner &
10 Pfleiderer.

The compounder may be supplied with the dry-compacted calcium carbonate which has been densified at a different location. However, in one embodiment of the invention, the calcium carbonate is densified upstream
15 of the compounder and then supplied direct to the compounder, for example via a suitable conveyor means. Alternatively, the compactor may be disposed such that the compacted calcium carbonate is supplied directly to the compounder. For example, the outlet from the
20 compactor may be disposed vertically above the inlet to the compounder. An arrangement is shown in Figure 2 which includes a conveyor means between the compactor and the compounder. The apparatus represented in Figure 2 comprises a compactor 1 for dry-compacting or
25 densifying a source of particulate calcium carbonate supplied to it, a compounder 2 for compounding the particulate calcium carbonate and the polymer, and a packaging means 3 for packaging the filled polymer composition obtained. The compactor 1 is capable of
30 compacting the calcium carbonate to a bulk density

- 10 -

greater than the maximum bulk density obtainable by
subjecting an uncompacted sample of the calcium
carbonate to tamping. The compounder 2 includes a first
inlet for receiving a flow of a polymer (via line 4) and
5 a second inlet for receiving the dry compacted calcium
carbonate from the compactor 1 via line 5. The
densified calcium carbonate from the compactor 1 is
supplied to the compounder via a conveyor 6 which is
located between the compactor 1 and the second inlet to
10 the compounder 2. As an alternative to the packaging
means, the filled polymer may be stored and then shipped
in bulk or in suitable receptacles, such as bags. As
previously indicated, the process of the first aspect of
the invention result in a calcium carbonate-filled
15 thermoplastic polymer composition which is useful in the
manufacture of breathable film. Typically, the
composition resulting from the process of the first
aspect of the invention will be in the form of a
concentrate or masterbatch from which the breathable
20 film is then manufactured, normally in a process which
is carried out at a location separate from the location
of the manufacture of the composition.

The process employed to form the intermediate film
product, and subsequently the stretched polymer film,
25 from the thermoplastic material and the particulate
calcium carbonate may be one or more of the methods well
known in the art as described later.

The masterbatch or concentrate, e.g. in the form of
pellets, is melted and extruded or shaped into the
30 intermediate film (i.e. the film before stretching) by

- 11 -

the use of a suitable film forming machine, as well known in the art. Normally, the masterbatch, prior to the film forming step is "let down" to a suitable calcium carbonate content, using a polymer which may be the same as or different from the polymer of the masterbatch. For example, the masterbatch may be formed at a mineral filler content of the order of 70 wt.% which is let down to a mineral filler content of, for example, 55 wt.%

10 The intermediate film may be a blown film, cast film or extruded film. Other types of films are also considered to be within the scope of the present invention provided the forming technique is compatible with filled films. Appropriate methods for producing the films according to the present invention will be readily apparent to the skilled artisan.

The intermediate film is then heated, e.g. to a temperature of about 5°C less than about the melting point of the thermoplastic polymer or more, and then stretched to at least about 1.2 times, preferably at least 2.5 times, its original length to thin the film and render it porous.

An additional feature of the thinning process is the change in opacity of the film. As formed, the film is relatively transparent but after stretching, it becomes opaque. In addition, while the film becomes orientated during the stretching process, it also becomes softer. Taking all these factors into consideration, and the desire to have a water vapor transmission rate of at least 100 grams per square meter

- 12 -

per 24 hours, the film may, for example, be thinned to such an extent that it has a weight per unit area of less than about 35 grams per square meter for personal care absorbent article applications and a weight per unit area of less than about 18 grams per square meter for certain other applications.

The film forming machine may for example comprise an extruder equipped with a T-die or the like or an inflation molding machine equipped with a circular die.

10 The film production may be carried out at some time after the masterbatch production, possibly at a different manufacturing plant. In some cases, the masterbatch can directly be formed into the film without producing an intermediate product.

15 The film can be stretched in at least a uniaxial direction at a temperature of from room temperature to the softening point of the thermoplastic polymer in a known manner such as a roll method, an interdigitizing method, or a tenter method to bring about the

20 interfacial separation of the polymer and the filler from each other, whereby a porous film can be prepared. The stretching may be carried out by one step or by several steps. Stretch magnification determines film breakage at high stretching as well as breathability and

25 the moisture vapor transmission of the obtained film, and so excessively high stretch magnification and excessively low stretch magnification are desirably avoided. The stretch magnification is preferably in the range of 1.2 to 5 times, more preferably 1.2 to 4 times

30 in at least a uniaxial direction. If biaxial stretching

- 13 -

is carried out, it is possible that for example stretching in a first direction is applied in the machine direction or a direction perpendicular thereto, and stretching in a second direction is then applied at right angles to the first direction. Alternatively, the biaxial stretching may be carried out simultaneously in the machine direction and the direction perpendicular thereto. Any method known in the art or after developed can be applied in making the film in the method according to this aspect of the present invention.

After the stretching, a heat setting treatment may be carried out if required in order to stabilize the shape of obtained voids. The heat setting treatment may be, for example, a heat setting treatment at a temperature in the range of from the softening point of the resin to a temperature less than about the melting point of the resin for a period of 0.1 to 100 seconds.

No particular restriction is put on the thickness of a breathable film produced of the present invention. The thickness should be such as to obtain film unlikely to tear or break and which has appropriate softness and good feel. Usually, the thickness of the breathable film is in the range of 5 μm to 100 μm , preferably 10 μm to 70 μm .

Generally, once the film is formed, it will have a weight per unit area of less than about 100 grams per square meter and after stretching and thinning its weight per unit area will be less than about 35 grams per square metre and more desirably less than about 18 grams per square metre.

- 14 -

For the purposes of the present invention, a film is "breathable" if it has a water vapour transmission rate (WVTR) of at least 100 g/m²/24 hours as calculated using the test method described in US Patent No.

5 5,695,868.

In this specification, "film" means a sheet or layer of material having a median thickness of no more than about 250 µm. Typical thickness sizes and properties of films are described later. The film of
10 the present invention is a breathable film, i.e. having microscopic interconnecting pores not greater than about 30 µm in size (usually much less). Such a film allows for example water vapor in the atmosphere on one side of the film to permeate to the atmosphere on the other side
15 without liquid water being transmitted through the film.

The calcium carbonate used in the present invention may comprise a carbonate obtained from a mineral source and processed by refining and treatment processes including grinding to obtain a suitable particle size
20 distribution. The grinding process may be carried out either in a dry state in the absence of added hygroscopic or hydrophilic chemicals or in a wet state in an aqueous medium in which any dispersant employed is minimized and/or subsequently removed from the filler in
25 a known manner. Wet ground material is subsequently dried to an extent such that the particulate material has an appropriate moisture content. The particles of the particulate product according to the present invention are treated (coated) with one of the aliphatic

carboxylic acid hydrophobizing surface treatment agents conventionally employed to coat carbonates.

Such a carbonate may be obtained from a natural source, e.g., marble, chalk, limestone or dolomite, or
5 may be prepared synthetically, e.g., by reaction of carbon dioxide with an alkaline earth metal hydroxide, e.g., calcium hydroxide, or may be a combination of the two, i.e., naturally derived and synthetic material. Desirably, at least 95%, preferably at least 99%, by
10 weight of the inorganic particulate material comprises alkaline earth metal carbonate although minor additions of other mineral additives, e.g., one or more of kaolin, calcined kaolin, wollastonite, bauxite, talc or mica, could also be present together with the carbonate. At
15 least 95% to 99% by weight may be calcium carbonate which may be obtained in a well known way by processing naturally occurring calcium carbonate obtained from a mineral source or by chemical synthesis, e.g., from the reaction of carbon dioxide and lime (calcium hydroxide).

20 The particulate product according to the present invention preferably has one or more of the following particle size properties:

- i. a mean particle size (approximately equal to the value d_{50}) of from about 0.5 μm to 10 μm ,
25 especially from about 0.5 μm to 5 μm , e.g., from about 0.8 μm to 3 μm ;
- ii. a top cut (the particle size value less than about which at least 99% by weight of the particles of the material have a size) of less

- 16 -

- than about 10 μ m, desirably less than about 8 μ m;
- iii. a specific surface area of from 3 m².g⁻¹ to 6 m².g⁻¹ as measured by the BET nitrogen absorption method;
- iv. a moisture pick up of less than about 0.35% by weight, more preferably less than about 0.2 % by weight, and most preferably less than about 0.1% by weight;
- v. a loss on ignition value of less than about 1.3 %, more preferably less than about 1.1%, and most preferably on the order of about 1.0%.

All particle size values as specified herein are measured by the well known conventional method employed in the art of sedimentation of the particles in a fully dispersed state in an aqueous medium using a SEDIGRAPH 5100 machine as supplied by Micromeritics Corporation, USA.

The calcium carbonate used in the present invention preferably has a total surface moisture content which is preferably less than about 0.1% by weight even after exposure for 40 hours at 20°C to a moist atmosphere having a relative humidity of 80%. Desirably, the surface moisture content is less than about 0.1% by weight even after exposure for 40 hours at 20°C to an atmosphere having a relative humidity of 97%.

The calcium carbonate filler used in the present invention may be ground to obtain a suitable particle size distribution. The grinding process may be carried

- 17 -

out either in a dry state in the absence of added hygroscopic or hydrophilic chemicals or in a wet state in an aqueous medium in which any dispersant employed is minimized and/or subsequently removed from the filler in a known manner. Wet ground material is subsequently dried to an extent such that the particulate material has an appropriate moisture content.

The calcium carbonate used in the invention may have been processed, e.g. by known purification, comminution and particle size classification procedures to have a suitable form prior to use to form the particulate product according to the present invention. However, following such processing the amount of hygroscopic or hydrophilic additives present is preferably minimized, as described earlier, e.g. by removing any such additives used by a washing process.

The calcium carbonate used in the present invention is treated with a hydrophobizing surface treatment agent and the treatment may be carried out prior to use by addition to thermoplastic polymeric material. Alternatively, the hydrophobizing agent, sometimes referred to as antagonizing agent, may be added directly to the thermoplastic polymer with which the calcium carbonate is to be compounded, before, during or after addition of the particulate product according to the present invention. For maximizing the effect of the hydrophobizing agent, complete surface treatment of the calcium carbonate is preferred prior to addition to the thermoplastic polymer.

Use of surface treatment agents, which, when added to the inorganic particulate material which is dry, facilitate dispersion of the inorganic particulate material in hydrophobic polymeric material are well known. Suitable surface treatment agents are known to include aliphatic carboxylic acids having from 10 to 30 carbon atoms in their chain, including but not limited to, stearic acid, behenic acid, palmitic acid, arachidic acid, montanic acid, capric acid, lauric acid, myristic acid, isostearic acid and cerotic acid and mixtures thereof.

Further details concerning the surface treatment of calcium carbonate fillers for polymer compositions may be found in WO 99/61521, the contents of which are incorporated herein by reference for all purposes.

The production route employed for producing the calcium carbonate used in the present invention can be selected from the many procedures known to those skilled in the art.

Again, further details regarding the production of suitable particulate calcium carbonate minerals for use in the invention may be found in WO 99/61521, the contents of which are incorporated herein by reference for all purposes. In the intermediate film product and the subsequent stretched product, the thermoplastic polymer may form from 20% to 80% by weight and the filler will form from 20% to 80% by weight of the composition, i.e. combination of the polymer plus filler. More preferably, the thermoplastic polymer forms from about 30% to about 55% by weight of the

- 19 -

composition and the filler forms from about 45% to about 70% by weight of the composition.

The preferred thermoplastic polymer for use in the invention is a thermoplastic polyolefin, for example one
5 which comprises more than about 50% by weight of olefin units and is sometimes referred to as polyolefin resin.

The polyolefin polymers (or resins) which can be used to provide the polyolefin resin, for example, include mono-olefin polymers of ethylene, propylene,
10 butene or the like, or copolymers thereof as a main component. Typical examples of the polyolefin resin include polyethylene resins such as a low-density polyethylene, linear low-density polyethylene (ethylene- α -olefin copolymer), middle-density polyethylene and
15 high-density polyethylene; polypropylene resins such as polypropylene and ethylene-polypropylene copolymer; poly(4-methylpentene); polybutene; ethylene-vinyl acetate copolymer; and mixtures thereof. These polyolefin resins may be obtained by polymerization in a
20 known way, e.g. by the use of a Ziegler catalyst, or obtained by the use of a single site catalyst such as a metallocene catalyst. Above all, polyethylene resins are preferable, and linear low-density polyethylene (ethylene- α -olefin copolymer) and low-density
25 polyethylene are most preferable. Furthermore, in view of the extrudability, the stretchability and the like of the film, the melt index of the polyolefin resin is preferably in the range of about 0.5 to 5 g/10 min.

- 30 -

pressure sufficient to increase the bulk density above the maximum bulk density obtainable by subjecting an uncompact sample of the calcium carbonate to tamping.

7. A process according to claim 6, wherein the
5 calcium carbonate is subjected to pressure by being passed between a pair of rotating rollers.

8. A process according to claim 6 or 7, wherein the starting calcium carbonate is also subjected to deaeration.

10 9. A process for making a composition which comprises a polymer and a particulate calcium carbonate filler, said process comprising:

supplying the polymer and the calcium carbonate filler to a compounder for compounding the filler and
15 the polymer; and

compounding the filler and polymer to form a uniform dispersion composition in which the calcium carbonate is uniformly dispersed in the polymer;

wherein the calcium carbonate filler is supplied to
20 the compounder in a dry compacted form which has a bulk density greater than the maximum bulk density obtainable by subjecting an uncompact sample of the calcium carbonate to tamping

10. A process according to claim 9, wherein the
25 thermoplastic polymer is a polyolefin polymer.

11. A process according to claim 9, wherein the calcium carbonate has a bulk density which is at least 50g/litre greater than the tamped bulk density.

- 31 -

12. A process according to claim 9, wherein the calcium carbonate has a bulk density which is at least 100g/litre greater than the tamped bulk density

13. A process according to claim 9, wherein the
5 calcium carbonate has a bulk density which is at least 150g/litre greater than the tamped bulk density.

14. A process according to any one of claims 9 to 14, wherein the compacted calcium carbonate is obtained by subjecting a starting calcium carbonate to the action
10 of pressure sufficient to increase the bulk density above the maximum bulk density obtainable by subjecting an uncompacted sample of the calcium carbonate to tamping.

15. A process according to claim 14, wherein the
15 calcium carbonate is subjected to pressure by being passed between a pair of rotating rollers.

16. A process according to claim 14 or 15, wherein the starting calcium carbonate is also subjected to deaeration.

20 17. An apparatus for making a calcium carbonate-filled thermoplastic polymer composition comprising:

a compactor for dry-compacting a source of particulate calcium carbonate supplied to it, said compactor being capable of compacting the calcium
25 carbonate to a bulk density greater than the maximum bulk density obtainable by subjecting an uncompacted sample of the calcium carbonate to tamping; and

an extruder which includes at least one inlet
30 for receiving the dry compacted calcium carbonate

Other thermoplastic polymers which may be used in the practice of the present invention are thermoplastic elastomers, such as SBS.

Desirably, the filler includes at least 50% by weight, e.g. from 80% to 99% by weight of the calcium carbonate where one or more other fillers are employed together with the particulate product according to the present invention. Where another filler is employed, this may be co-compacted with the calcium carbonate or
10 may be added separately to the thermoplastic polymer.

Examples of the other fillers include barium sulphate, calcium sulphate, barium carbonate, magnesium hydroxide, aluminum hydroxide, zinc oxide, calcium oxide, magnesium oxide, titanium oxide, silica and talc.
15 The average particle diameter of the other filler is preferably 20 μm or less, preferably 10 μm or less, preferably in the range of 0.5 to 5 μm . In order to improve the dispersibility of the other filler in the polymer, the other filler may be subjected to a surface
20 treatment to render its surfaces hydrophobic, may be used. Examples of suitable surface treatment agents include the fatty acids such as stearic acid, specified earlier.

In the preparation of a breathable film according
25 to the present invention, one or more other fillers may be employed together with the ground calcium carbonate filler. In order to improve the dispersibility of the other filler in the thermoplastic polymer, the other filler or fillers may be subjected to a surface
30 treatment to render its surfaces hydrophobic. Examples

- 21 -

of suitable surface treatment agents include the fatty acids such as stearic acid, as mentioned earlier.

The composition ratio between the thermoplastic polymer and the calcium carbonate filler has an influence on the extrudability and the stretchability of the film as well as the breathability and the moisture vapor transmission of the obtained film. If the amount of the filler is insufficient, adjacent micropores, which are required to be obtained by the interfacial separation of the polymer and the calcium carbonate filler from each other, are not continuous, so that a porous film having good gas breathability and moisture vapor transmission cannot be obtained. On the contrary, if the amount of the calcium carbonate filler is excessive, defective extrusion occurs during the film forming process and the stretchability deteriorates, so that the sufficient stretching cannot be carried out. In view of these limiting factors, the composition ratio between the polymer and the calcium carbonate filler may be from 25 to 70 parts by weight of the polymer with respect to from 75 to 30 parts by weight of the calcium carbonate filler, e.g. from 30 to 60 parts by weight of the polymer with respect to 70 to 40 parts by weight of the calcium carbonate filler.

The breathable film can be suitably utilized in applications requiring softness, for example, as the backing sheet of disposable diapers.

"Porous" as used in the present application includes but is not coextensive with "breathable" films.

- 22 -

No particular restriction is put on the lower limit of the softness, but it is usually about 20 mm.

A breathable film of the present invention having such properties may have a suitable breathability, moisture vapor transmission and feeling as well as excellent mechanical properties and long-term adhesive properties to be suitably used in products such as disposable diapers, body fluid absorbing pads and bed sheets; medical materials such as surgical gowns and base materials for hot compress; clothing materials such as jumpers, rainwear; building materials such as wallpapers and waterproof materials for roofs and house wraps; packaging materials for packaging desiccants, dehumidifying agents, deoxidizers, disposable body warmers; packaging materials for keeping the freshness of various articles and foods; separators for the cells; and the like. The breathable film is particularly desirable as a material used in products such as disposable diapers and body fluid absorbing pads. The breathable film may in such products be formed into a composite or laminate in one of the ways well known in the art with one or more other layers, e.g. a non-woven fibrous layer, e.g. by an adhesive or bonding agent.

Embodiments of the present invention will now be described, by way of example only, and with reference to the following Examples.

Examples

Two particulate calcium carbonates were densified on a hand-operated densifier apparatus (Universal Processes and Plant Limited, Model 160/220). Calcium carbonate A was a ground calcium carbonate having a hydrophobic surface coating and d_{50} of $2.00\mu\text{m}$ and a tamped bulk density (obtained using the procedure set forth in Appendix A) of 1400g/litre . Calcium carbonate B was a ground calcium carbonate having a hydrophobic surface coating and a d_{50} of $1.3\mu\text{m}$ and a tamped bulk density (obtained using the procedure set forth in Appendix A) of 1300g/litre . The bulk density of the densified products obtained is shown in Table 1.

Table 1

Run	Calcium Carbonate	Feedrate Kg/hr	Vacuum in Hg	Drum speed (rpm)	Gap (mm)	Product bulk density G/l
1	A	940	10	7	7	1500
2	A	489	15	5	8	1550
3	A	372	26	5	5	1550
4	A	306	26	5	5	1550
5	B	540	25	5	4	1350
6	B	-	25	5	3	1450

Control calcium carbonates (A and B without densification treatment) and the densified calcium carbonates were compounded with an LLDPE having a MFR of $2.3\text{g}/10\text{ min}$ on a Werner and Pfleiderer ZSK-40 twin screw extruder to produce a masterbatch containing 70 wt.% calcium carbonate. The calcium carbonate was fed via a side feeder from a gravimetric hopper approximately 2 m above the extruder. The screw speed was maintained at 300 rpm, and the throughput increased incrementally

- 24 -

until some limit was reached, either physical or mechanical. The processing conditions used are summarised in Figures 3a-3e.

As illustrated by Figure 3a, the thrust reading (% torque to the clutch) for Control B was higher than the densified material.. At higher throughputs (> 120 kg/h) the thrust reading for the Control A was slightly higher than those for the densified material.

As illustrated by Figure 3b, the melt pressure was highest for Control B. A high degree of scatter was seen with the other masterbatch data, with some anomalous readings for one of the densified carbonate A samples. At higher throughputs the melt pressures for Control A and the densified material were comparable.

As illustrated by Figure 3c, the calculated work inputs for Control B and the densified carbonate B were comparable. At the highest throughput rates the work input for two of the densified carbonate A samples was slightly lower than the control, with the highest work input result seen for the other of the densified carbonate A samples.

As illustrated by Figure 3d, the work output for Control B was marginally higher than that calculated for the densified material. At lower throughputs the work output results for all the densified carbonate A samples were comparable. At higher throughputs the densified carbonate A samples had slightly lower work output rates than the control.

As illustrated by Figure 3e, the drive command data (giving an indication of ease of flow of the material

through the screw) for Control B showed no trends. However, the percentage drive input for the densified carbonate B was lower at all throughput rates. At lower throughput rates the drive command for all the densified carbonate A samples products was lower. No differences were observed at higher outputs (> 130 kg/h).

Each of the maximum throughput masterbatches (100 kg/h for densified carbonate B and 140 kg/h for densified carbonate A) was dried at 60°C overnight in a Conair-Churchill desiccant drier. The six masterbatches were let down in an LDPE having a MFR of 2g/10 min on a Betol BK 32 film extruder to produce 55 wt.% filled films (30 μm gauge). Die temperature was 220°C , screw speed was 56 RPM and the haul-off was 10 m min^{-1} . The dispersion of the calcium carbonate was assessed by placing each film over a light box and counting the agglomerates. Four 1 m lengths, 225 mm layflat, were measured and a mean value obtained. The results obtained are set forth in Table 2 below.

Table 2

Sample from Run	Output Rate (kg/h)	Defect count (per m^2)
Control B	100	> 445
Run 6	100	227
Run 6	110	129
Control A	140	111
Run 1	140	102
Run 2	140	49
Run 3	140	44

The number of film defects was highest with Control B. This could have been due in part to some minor contamination from the die (since this was the first

material run through the film line). The densified products, both for carbonate A and B, had fewer film defects than the respective control, with increasing densification levels causing a reduction in defects.

- 5 The masterbatch output also affected defect levels. With an increase in throughput from 100 to 110 kg/h for the densified carbonate B, the number of defects was approximately halved.

Appendix ATamping Procedure

- 5 This procedure may be used to determine the maximum bulk density obtainable by tamping a sample of a calcium carbonate filler material.

Equipment

10

- Tamping apparatus (described in more detail below).
- Graduated measuring cylinder having a capacity of 50ml and a bung to fit.
- Balance to weigh $1000g \pm 0.01g$
- 15 • Palette knife or spatula.

The tamping apparatus is shown in Figure 1 and comprises a rotatable cam 10 adapted to support the measuring cylinder 11 (supported by a support means (not shown) and which includes a cut away portion 12 to provide a sudden vertical fall of 2.5cm. The apparatus includes a counter (not shown) to count the number of revolutions of the shaft 13 on which the cam rotates, and hence "jolts" to the cylinder. The shaft 13 rotates at about 60rpm.

Method

1. Tare the weight of the measuring cylinder.
- 30 2. Fill the measuring cylinder to approximately 50ml
3. Level the contents of the cylinder with the palette knife or spatula
4. Weigh the cylinder and record the nett weight of the contents
- 35 5. Fit the bung into the measuring cylinder and attach the cylinder to the packing apparatus
6. Set the counter of the tamping apparatus to 500 counts and switch on.
7. After 500 counts note the volume of the test material
- 40 8. Set the counter of the tamping apparatus to 100 counts, switch on and note the volume of the test material after 100 counts.

9. If the volume of the test material has changed,
repeat step 8 until no further change in volume is
obtained.
10. Record the final volume of the test material.

5

Expression of Results

The maximum bulk density is expressed as g/cm^3 and is
calculated as follows:

10

$$\text{Bulk Density} = W/V$$

where W is the nett weight of the test material
recorded in step 4 and V is the final volume of the test
material recorded in step 10.

15

- 29 -

CLAIMS:

1. A process for incorporating a particulate calcium carbonate filler in a thermoplastic polymer to form a calcium carbonate-filled polymer composition
5 suitable for the preparation of breathable polymer film, said process comprising:
- (a) introducing the calcium carbonate
into the polymer in a dry compacted
form which has a bulk density
10 greater than the maximum bulk
density obtainable by subjecting an
uncompacted sample of the calcium
carbonate to tamping; and
- (b) mechanically treating the polymer to
15 disperse the calcium carbonate
uniformly therein.
2. A process according to claim 1, wherein the thermoplastic polymer is a polyolefin polymer.
3. A process according to claim 1, wherein the
20 calcium carbonate has a bulk density which is at least
50g/litre greater than the tamped bulk density.
4. A process according to claim 1, wherein the calcium carbonate has a bulk density which is at least
100g/litre greater than the tamped bulk density
- 25 5. A process according to claim 1, wherein the calcium carbonate has a bulk density which is at least
150g/litre greater than the tamped bulk density.
6. A process according to any preceding claim,
wherein the compacted calcium carbonate is obtained by
30 subjecting a starting calcium carbonate to the action of

- 32 -

from the compactor and a flow of a thermoplastic polymer;

wherein the compactor is disposed to supply the compacted calcium carbonate to the compounder.

5 18. An apparatus according to claim 17, wherein the compactor has an outlet from which the compacted calcium carbonate is discharged, said outlet being located such that it may discharge the compacted calcium carbonate directly to the inlet to the compounder.

10 19. An apparatus according to claim 17, further comprising at least one conveyor located between the compactor and the inlet to the compounder for conveying the compacted calcium carbonate to the compounder.

1/5

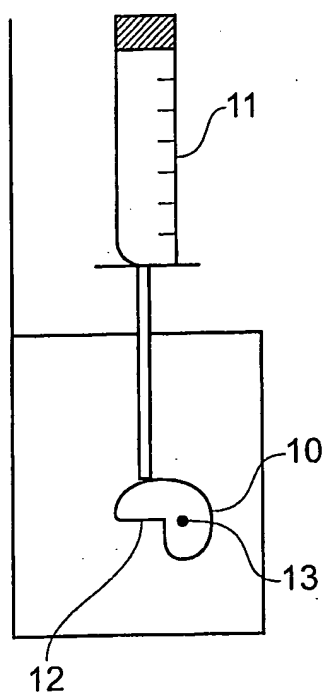


Fig. 1

2/5

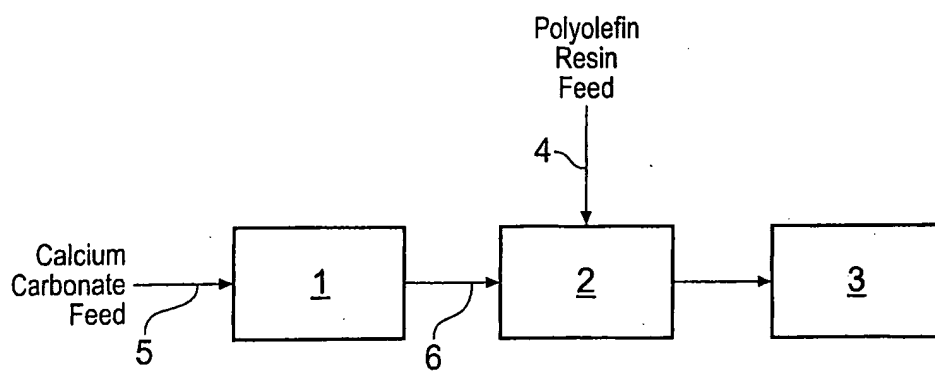


Fig. 2

3/5

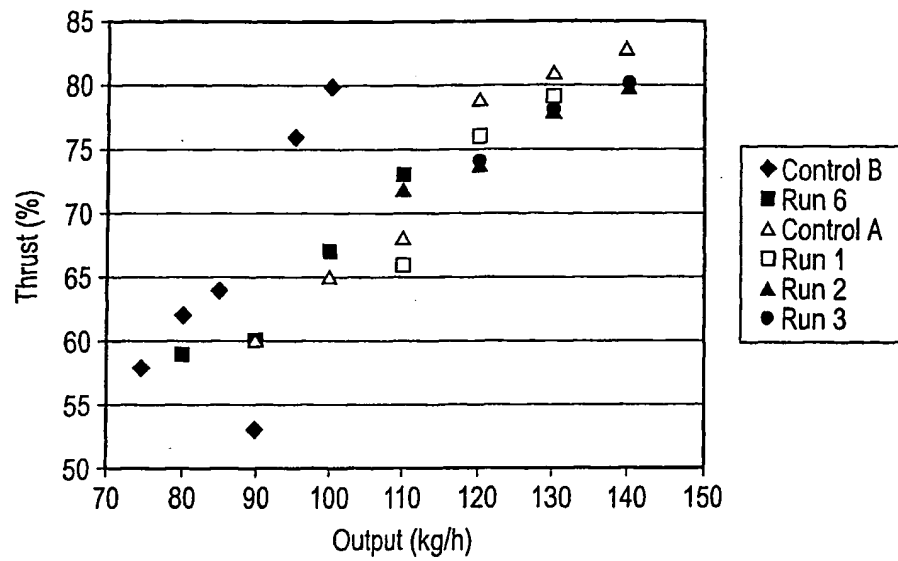


Fig. 3a

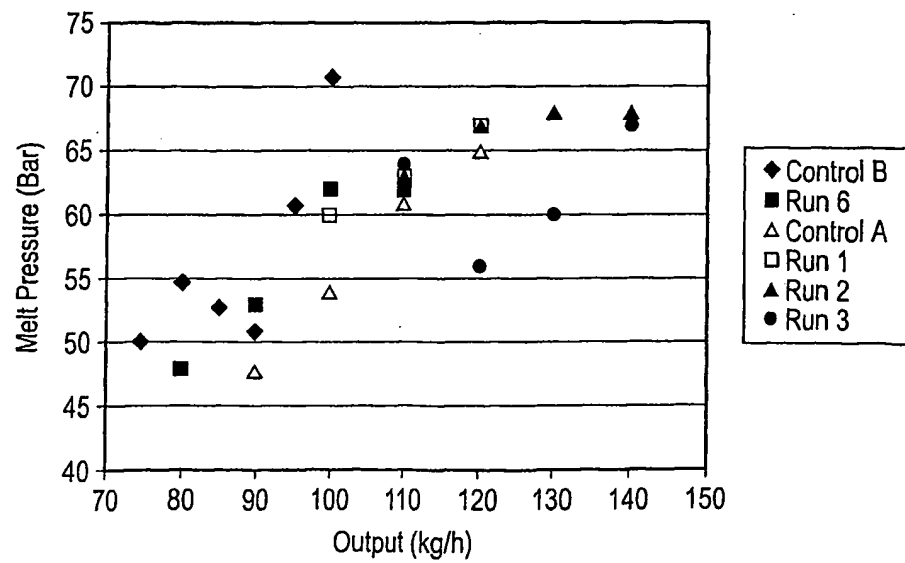


Fig. 3b

4/5

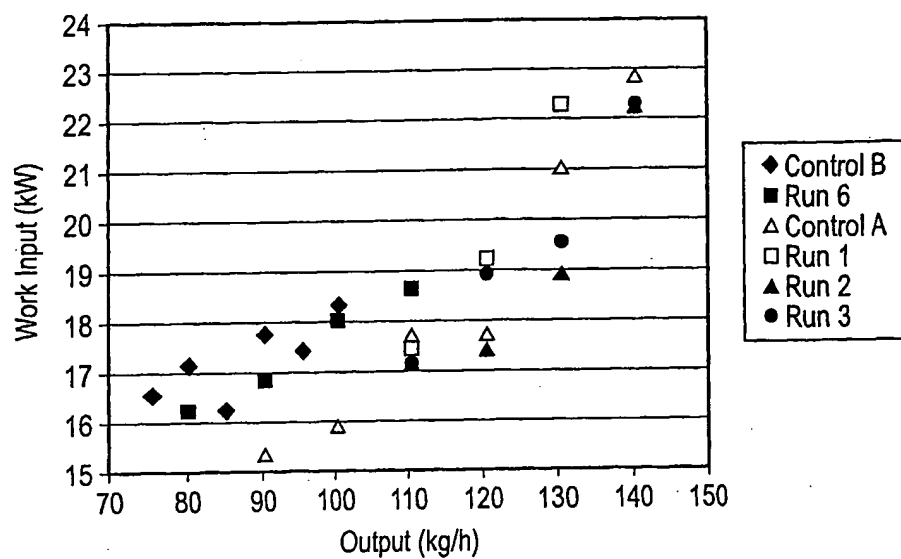


Fig. 3c

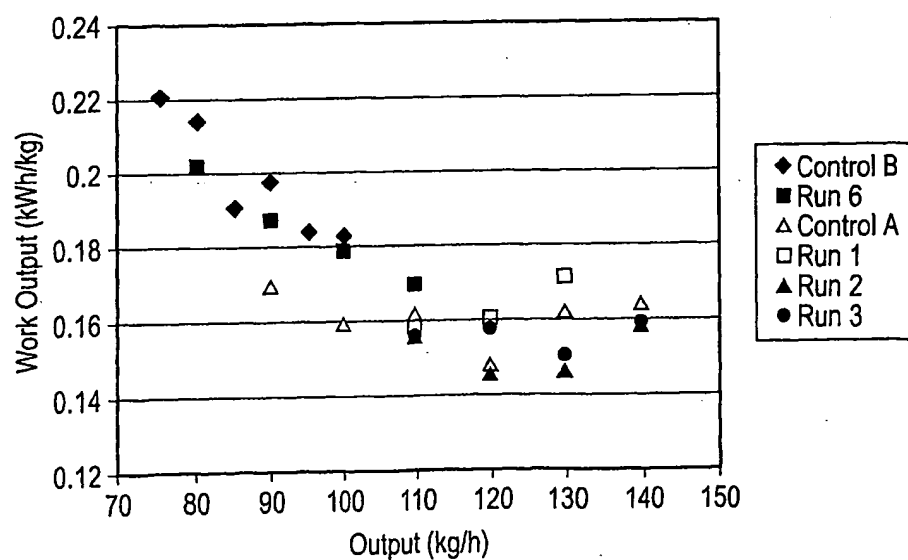


Fig. 3d

5/5

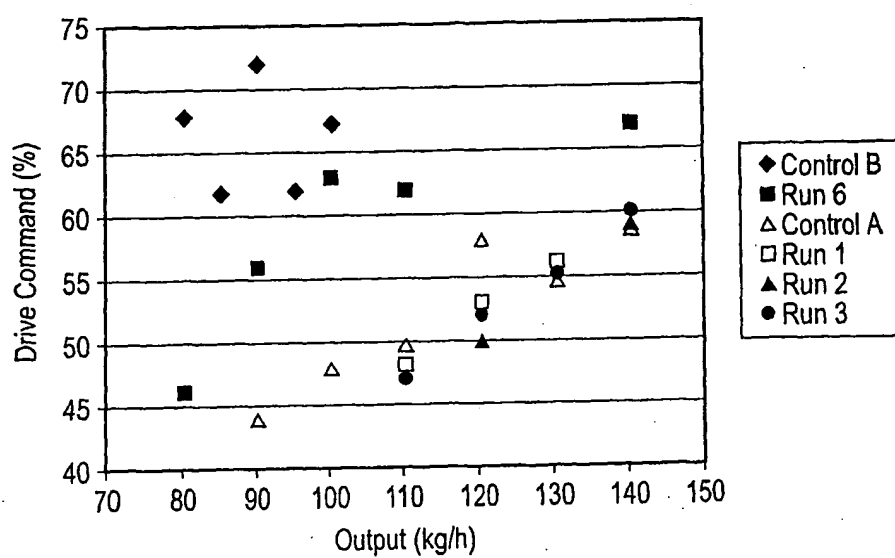


Fig. 3e

INTERNATIONAL SEARCH REPORT

PCT/GB 02/04599

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 B29B15/08 B29C47/10 //B29K23:00,B29K105:04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B29B B29C C08J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 239 197 B1 (INCHLEY PAUL EDWARD ET AL) 29 May 2001 (2001-05-29) claims 1,13,17	1-17
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 09, 31 July 1998 (1998-07-31) & JP 10 100144 A (KURIMOTO LTD), 21 April 1998 (1998-04-21) abstract	18-20
A	PATENT ABSTRACTS OF JAPAN vol. 009, no. 096 (C-278), 25 April 1985 (1985-04-25) & JP 59 226014 A (MITSUI MOKUZAI KOGYO KK), 19 December 1984 (1984-12-19) abstract	1

-/-



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

6 January 2003

Date of mailing of the international search report

16/01/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

Van Nieuwenhuize, O

INTERNATIONAL SEARCH REPORT

PCT/GB 02/04599

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 827 917 A (FOURTY GEORGES) 27 October 1998 (1998-10-27) cited in the application claim 1 ----	1
A	US 5 773 503 A (STEEN WILLIAM P ET AL) 30 June 1998 (1998-06-30) cited in the application claim 1 ----	1
A	WO 99 61521 A (ANSARI DEEBA MARJAN ;ECC INT LTD (GB); SHURLING DICKEY S (US); CAL) 2 December 1999 (1999-12-02) cited in the application the whole document ----	1
A	US 5 695 868 A (MCCORMACK ANN LOUISE) 9 December 1997 (1997-12-09) cited in the application the whole document ----	1
A	US 4 904 285 A (NAKAYAMA MAMORU ET AL) 27 February 1990 (1990-02-27) claim 1; figure 1 ----	18
A	US 5 580 537 A (SEXTL GERHARD ET AL) 3 December 1996 (1996-12-03) claim 1 -----	18

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/GB 02/04599

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6239197	B1	29-05-2001	AU 4361800 A WO 0064966 A1	10-11-2000 02-11-2000
JP 10100144	A	21-04-1998	NONE	
JP 59226014	A	19-12-1984	NONE	
US 5827917	A	27-10-1998	FR 2714326 A1 AT 171102 T AU 1319595 A CA 2178336 A1 DE 69413419 D1 DE 69413419 T2 EP 0737123 A1 ES 2123232 T3 FI 962675 A WO 9517998 A1	30-06-1995 15-10-1998 17-07-1995 06-07-1995 22-10-1998 27-05-1999 16-10-1996 01-01-1999 28-06-1996 06-07-1995
US 5773503	A	30-06-1998	NONE	
WO 9961521	A	02-12-1999	AU 3938399 A CA 2303812 A1 EP 0998522 A1 WO 9961521 A1	13-12-1999 02-12-1999 10-05-2000 02-12-1999
US 5695868	A	09-12-1997	AU 687967 B2 AU 1335395 A BR 9408329 A CA 2116081 A1 CN 1142798 A DE 9422432 U1 DE 69417258 D1 DE 69417258 T2 EG 20760 A EP 0734321 A1 ES 2131800 T3 FR 2713983 A1 FR 2717737 A1 GB 2285408 A ,B JP 9506656 T PL 315183 A1 RO 116364 B1 RU 2140855 C1 WO 9516562 A1 US 5855999 A ZA 9410026 A	05-03-1998 03-07-1995 19-08-1997 18-06-1995 12-02-1997 24-01-2002 22-04-1999 08-07-1999 31-01-2000 02-10-1996 01-08-1999 23-06-1995 29-09-1995 12-07-1995 30-06-1997 14-10-1996 30-01-2001 10-11-1999 22-06-1995 05-01-1999 22-08-1995
US 4904285	A	27-02-1990	JP 1299640 A JP 7047120 B JP 1139138 A JP 2042877 C JP 7063616 B CA 1309954 A1 DE 3825950 A1 FR 2618694 A1 GB 2208378 A ,B KR 9305297 B1	04-12-1989 24-05-1995 31-05-1989 09-04-1996 12-07-1995 10-11-1992 16-02-1989 03-02-1989 30-03-1989 17-06-1993

INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/GB 02/04599

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5580537	A	03-12-1996	DE 4309995 A1	29-09-1994
			AT 140653 T	15-08-1996
			AU 671714 B2	05-09-1996
			AU 5909394 A	29-09-1994
			DE 59400438 D1	29-08-1996
			DK 618065 T3	25-11-1996
			EP 0618065 A1	05-10-1994
			ES 2092340 T3	16-11-1996
			GR 3020727 T3	30-11-1996
			JP 2519021 B2	31-07-1996
			JP 7001198 A	06-01-1995
			KR 167807 B1	15-01-1999
			US 5711215 A	27-01-1998